UDC 666.63:691.58:547.001.5

CORRELATION OF PROPERTIES OF COMPOSITE MATERIALS BASED ON SILOXANE BINDER WITH THE TYPE OF FILLER

I. M. Yao[1] and O. S. Sirotkin[1]

Translated from Steklo i Keramika, No. 5, pp. 26 – 28, May, 2000.

Composite ceramic materials are produced by the sol-gel method, based on siloxane binder and finely disperse powders of high-melting fillers (based on various borides, nitrides, and carbides) which do not require lengthy sintering at high temperatures. It is established that the best filler is AlN, and after heat treatment at 900°C material based on this filler shows increased hardness, strength, and heat stability.

The need for development of more cost-effective engineering ceramic materials is making the sol-gel method for production of ceramics especially topical. This method is based on the use of various binders which allow for the production of ceramic-like composite materials either without firing, or under low-temperature treatment. The application of a polyorganosiloxane binder facilitates the uniform distribution of mixture components and the emergence of a thin enveloping binding film on the filler grain surface. The formation of the silica binding phase at increased temperatures significantly facilitates the sintering process in high-melting materials.

This technology is amply described in the technical literature [1 – 6]. For instance, the main attention in [1, 2] is focused on using the specified method to produce corundum materials. The authors note the formation of strengthening mullite "bridges" between individual Al_2O_3 particles in the course of sintering. The use of the sol-gel method to produce articles from SiC, grade M5, synthesized by the plasma-chemical method is described in [3].

The purpose of our study is to estimate the effect of fillers different in their chemical nature, as well as the filler dispersion, on the quality of composite ceramic materials (CCM) produced by the sol-gel method. In our study, we used finely disperse powders of the following high-melting fillers: Si_3N_4, AlN, BN, SiC, TiC, and TiB_2. All powders were obtained by the method of self-propagating high-temperature synthesis (SHS), and the average particle size was 1 – 7 μm. For reference purposes, we also used SiC powder of grade M50 synthesized by the plasma-chemical method and alumina, grade GLMK (99.8% α-Al_2O_3), with an average particle size up to 50 μm.

The binder component was a mixture of industrially produced organosilicon products: liquid caoutchouc CKTN-A (GOST 13835–73), ethyl silicate ETS-40 (GOST 26371–84), ethylsiloxane oligomer PES-5 (GOST 13004–77), and curing catalyst K-18 (TU 6.02805–75). The mixture was solidified at room temperature.

The processes taking place under high-temperature treatment of the material were studied using diffraction-thermal analysis (a MOM Paulik – Erdey derivatograph), and the phase composition of the product was identified by x-ray phase analysis (DRON-3). The microhardness of the heterophase material was determined with a PMT-3 instrument, and the physicochemical parameters of the obtained samples were measured by the standard methods.

The process of production of experimental cylindrical CCM samples of diameter and height 10 mm consists in the following stages: mixing the filler with the binder in the weight ratio 90 : 10 up to the formation of a homogeneous mixture; molding of samples under a pressure of 60 – 70 MPa with subsequent curing for 24 h at room temperature (to complete the cool curing process in the binder, as a consequence of which the samples acquire a certain initial strength); heat treatment of the samples at temperatures not exceeding 900°C. In doing so, the organic component of organosiloxanes is exothermically removed, and quartz and tridimite binding structures are formed on the filler particle surface and accordingly, between the particles, which provides for the strong skeleton of the material (DTA and x-ray phase analysis data).

Experimental samples of CCM based on the references powders (SiC or grade M50 and GLMK powder) did not produce desirable strength results, due to their coarse dispersion. The resulting materials crumbled away, which points to insufficient interphase adhesion at the phase boundary of the filler particles and siloxane macromolecules.

Samples based on silicon carbide and silicon nitride made by the SHS method on the whole exhibited satisfactory physicochemical parameters. As the silica binder formed on

[1] Kazan State Technological University, Kazan, Russia.

0361-7610/00/0506-0174$25.00

the particle surface starts sintering, a sufficiently strong frame is formed, which at 900°C achieves a compressive strength of 320 MPa for SiC and 250 MPa for Si_3N_4 (Table 1). At the same time, the internal structure of the material remains rather porous, since the content of the binder phase inside the material is insignificant. As a consequence of oxidation of the sample surface to SiO_2, a surface layer arises, which imparts additional strength and hardness to the material.

The material based on TiB_2 has relatively high strength characteristics. The compressive strength of some samples reached 500 MPa, which can be accounted by the emergence of a protective surface layer of high hardness, as well as the formation of the binder phase with strong adhesive effect inside the bulk of the material. A determining factor in the process of binding filler grains is not the silica phase, but oxidation of TiB_2 to boron oxide, whose melt has a wetting and binding capacity with respect to solid particles. Exposure at 950°C results in melting of B_2O_3 and binding of the entire bulk of the material by the vitreous phase, which imparts high strength to the material.

According to the x-ray phase analysis data, in heating to 900°C and holding for 20 min, titanium diboride gradually transforms into another, no less resistant solid crystalline compound, namely, $TiBO_3$ (the x-ray pattern shows the average interplanar distances typical of this compound). A protective yellow-colored coat consisting of crystalline titanium oxide (of the rutile type) emerges on the sample surface, and the presence of boron oxide is clearly registered inside the sample.

In the case of slow cooling, part of the B_2O_3 melt crystallizes mainly in the form of the cubic structure, thus binding individual TiB_2 and $TiBO_3$ grains in a monolithic heterophase material, whereas the remaining lesser part (or remaining larger part in the case of rapid chilling) remains amorphous. This is further evidenced by the vitrified "mirror" on the sample substrate after cooling, which points to the release of the low-melting melt from the sample.

Under a protracted high-temperature effect in air medium, the protective surface of TiO_2 becomes thicker, and the residual quantity of titanium diboride gradually transforms into $TiBO_3$, which later transforms as well to TiO_2 and low-melting B_2O_3. At temperatures 850 – 900°C, a weight increase was observed in the TiB_2 sample, due to the formation of complex compounds with oxygen, which leads to an increment in the initial powder weight.

Thus, TiB_2 under heat treatment produces a strong monolithic heterophase ceramic material with the clearly expressed crystalline phase $TiBO_3$ and the matrix vitreous phase B_2O_3.

The low strength of the composite based on hexagonal boron nitride (not more than 15 MPa) is also due to the formation of the protective surface film. This is presumably determined by weak interphase interaction of non-oxidized BN powder particles (exhibiting anti-adhesive properties) and the presence of the boron oxide binder phase.

TABLE 1

Properties of CCM after heat treatment at 900°C	Filler material				
	SiC	Si_3N_4	AlN	BN	TiB_2
Compression strength, MPa	320	250	550	15	500
Number of thermal cycles (900 – 20 – 900°C)	7	10	20	3	14
Microhardness, GPa	1.3	1.5	3.2	–	2.0

Samples based on boron carbide, on the contrary, exhibit a decrease in strength with increasing temperature, so that the samples disintegrate under the slightest load. In the course of heat treatment in air, the material is oxidized, CO and CO_2 are emitted, and individual TiO_2 particles are formed which are not bound in any way. The porous sample significantly loses its initial specific weight, its volume increases, and it becomes lightweight and fragile, whereas its color changes from black (TiC) to yellow (TiO_2).

Aluminum nitride samples have the highest compression strength (550 MPa). The reason for the high strength of the material based on aluminum nitride (with a small content of the binder phase SiO_2) was first attributed to the polymorphic phase transformation of AlN in the course of firing from the hexagonal syngony to the cubic syngony, which can strengthen the material. However, the x-ray patterns clearly register only the hexagonal phase of AlN, both before and after firing. No traces of impurities facilitating sintering were detected in the initial powder, nor any products of oxidation of AlN to Al_2O_3.

Significant drawbacks of the described technology of CCM production include anisotropy (nonuniformity) of the properties of the finished composite with respect to its thickness, shrinkage, and porosity values, which hampers the production of articles with guaranteed stable reproducibility of size and properties. In particular, such essential parameter as density of non-fired and heat-treated samples varied over a wide range. Elimination of these drawbacks and optimization of the technological parameters for manufacturing such CCM will make it possible to produce a material suitable for industrial use.

Such a composite material is needed in the case where the use of expensive ceramics is economically or technologically inexpedient, and other available composites cannot withstand thermal or other loads. Accordingly, this material will take an intermediate position between the traditionally made ceramics and the new materials developed on the basis of thermosetting binders and inert fillers. The practical application of such composite having acceptable hardness and high thermal resistance is feasible, for example, in nonferrous metallurgy in producing protective lining for electrolytic baths, or in machine and engine construction to produce wear-resistant end sealing rings for pumps and compressors, heat-resistant washers, bushings, and various insulating straps operating under the conditions of aggressive media, increased temperatures, or abrasive wear.

Thus, for the purpose of developing a less expensive engineering ceramic analog which does not require high-temperature sintering, samples of CCM based on polyorganosiloxane binder and various ceramic fillers were produced by the sol-gel method and investigated. It was established that the best filler is AlN, since after heat treatment at 900°C, the material based on this filler has substantial hardness, strength, and heat resistance.

REFERENCES

1. G. D. Semchenko, "Ultralight-weight ceramics using sol-gel compositions," *Steklo Keram.*, No. 5, 15 – 18 (1997).
2. S. V. Tishchenko, "Technological specifics of production of corrosion-resistant corundum ceramics," *Steklo Keram.*, No. 12, 12 – 13 (1990).
3. G. D. Semchenko, "Construction corundum ceramics with increased crack resistance," *Steklo Keram.*, No. 12, 16 – 17 (1990).
4. G. D. Semchenko, "Contemporary state of the use of sol-gel processes in ceramics technology," in: *Proceedings of the 16th Mendeleev Congr. on General and Applied Chemistry* [in Russian], Moscow (1998), p. 476.
5. L. P. Gurenko and M. S. Gurenko, "Nontraditional technology for improving heat resistance of corundum materials," in: *Proceedings of 16 Mendeleev Congress on General and Applied Chemistry* [in Russian], Moscow (1998), pp. 280 - 281.
6. G. D. Semchenko, *Sol-Gel Process in Ceramics Technology* [in Russian], Kharkov (1997).